Two–dimensional Copolymers and Multifractality:
Comparing Perturbative Expansions, MC Simulations, and Exact Results

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We analyze the scaling laws for a set of two different species of long flexible polymer chains joined together at one of their extremities (copolymer stars) in space dimension $D = 2$. We use a formerly constructed field–theoretic description and compare our perturbative results for the scaling exponents with recent conjectures for exact conformal scaling dimensions derived by a conformal invariance technique in the context of $D = 2$ quantum gravity. A simple MC simulation brings about reasonable agreement with both approaches. We analyse the remarkable multifractal properties of the spectrum of scaling exponents.

Polymers serve as a testing ground for a field theory since the early seventies [1, 2]. The path integral formulation [3] allows for a direct interpretation of the paths as conformations of random walks (RWs) and self avoiding walks (SAWs). Closed paths in this theory have a multiplicity of the number of components M of the field. The formal limit $M = 0$ excludes these loops and yields the polymer limit of field theory, that describes self and mutually interacting paths. The field theoretical description of the scaling properties of polymer chains in good solvents has been generalized to the case of multicomponent polymer solutions [4] and linked polymers [5, 6]. Recently, the theory was suited to describe polymer networks of different species [7, 8]. The simplest nontrivial case of a heterogeneous polymer network – a star-shaped copolymer in $D = 2$ dimensions – is the subject of the present report.

Polymer field theory usually has to be evaluated in terms of a truncated perturbation theory series. Obviously, it is always of special importance to compare these with the exact results if such exist. As a rule they are available for $D = 1, 2$. For the critical exponents that describe the scaling of homogeneous polymer chains and star polymers (or, more generally, homogeneous polymer networks) the perturbative approach [5] is in fair agreement with the exact data for $D = 2$ [6]. For the heterogeneous case however, only perturbative results [7, 8] were available until recently. An exact solution for scaling exponents has been recently proposed that uses methods of conformal invariance on random graphs [9]. Below we undertake a comparative analysis of the properties of the perturbative solution and of the exact one and complement these results by MC simulations. We show where the approaches agree and explain why they differ in general. In this respect our paper confirms some of the speculative results of [9] derived from the algebra of conformal dimensions for copolymer stars on $2D$ random graphs (quantum gravity).

A remarkable feature of the scaling spectrum of a copolymer star is that it possesses multifractal properties that can also be analyzed in terms of field theory and the conformal invariance approach. [7, 8, 9, 10, 11, 12].

a. *Copolymer stars and their scaling exponents* Star polymers as the most simple nontrivial examples of polymer networks [5, 6] are created by linking together the end points of polymer chains at a common core. Let us now consider a general star polymer made of chains of *two different species* (while all chains have equilibrium size R). When such a *copolymer star* is immersed in a good solvent its asymptotic properties are universal in the limit of long chains [1, 2, 3]. In particular, the number of configurations (the partition function Z_*) scales with R on some scale ℓ as:

$$Z_* \sim (R/\ell)^{-\lambda_{f_1, f_2}}, \qquad (1)$$

where λ_{f_1, f_2} constitute a family of copolymer star exponents [7, 8]. These are universal and depend only on the space dimension D and the number of chains of different species 1 and 2 (f_1 and f_2 correspondingly). If a nonvanishing mutual avoidance interaction is present between the chains of species 1 and 2 polymer field theory predicts two nontrivial physically different regimes [4] for the scaling behavior of true copolymer stars described by Eq. (1): In the first case the polymers of species 1 behave as RWs and the polymers of species 2 as SAWs, whereas in the second case both species display RW behavior [13]. For these two relevant cases a renormalization group description of the exponents λ_{f_1, f_2} has been given in terms of the scaling dimensions of appropriately composed composite operators of polymer field theory [7]. In particular, the resulting perturbation theory was derived in the form of an $\varepsilon = 4 - D$ expansion as well as evaluated directly for fixed D [14]. Following Ref. [7] where the copolymer star exponents η_{f_1, f_2}

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were calculated, the ε-expansion for the λ-exponents of a copolymer star composed of two mutually avoiding sets of RWs ($\lambda_{f_1,f_2}^G = -\eta_{f_1,f_2}^G$) and for a star of mutually avoiding sets of SAWs and RWs ($\lambda_{f_1,f_2}^U = -\eta_{f_1,f_2}^U + f_1\eta_{2,0}^U$) read:

$$\lambda_{f_1,f_2}^G(\varepsilon) = \frac{f_1 f_2 \varepsilon}{2}\{1 - (f_2 - 3 + f_1)\frac{\varepsilon}{4}[1 - (f_1 +$$
$$f_2 + 3\zeta(3) - 3)\frac{\varepsilon}{2}]\}, \tag{2}$$

$$\lambda_{f_1,f_2}^U(\varepsilon) = -f_1(3 - f_1 - 3f_2)\frac{\varepsilon}{8} - f_1(43 - 33f_1 +$$
$$8f_1^2 - 91f_2 + 42f_1 f_2 + 18f_2^2)\frac{\varepsilon^2}{256} - f_1[675 - 969f_1 +$$
$$456f_1{}^2 - 64f_1{}^3 - 2463f_2 + 2290f_1 f_2 - 492f_1{}^2 f_2 +$$
$$1050f_2{}^2 - 504f_1 f_2{}^2 - 108f_2{}^3 - \zeta(3)(712 - 936f_1 +$$
$$224f_1{}^2 - 2652f_2 + 1188f_1 f_2 + 540f_2{}^2)]\frac{\varepsilon^3}{4096}, \tag{3}$$

where $\zeta(3) \simeq 1.202$ is the value of the Riemann zeta function. While we do not display the exponents calculated at fixed space dimension D here explicitly, we show their numerical values below.

The perturbative formulas of the kind given in Eqs. (2)–(3) may be evaluated for $D = 3$ where the topological complexity of the problem does not allow for an exact treatment. One should be aware that for similar reasons an exact expression for the partition function Z_*, formula (1), can not be obtained for $D = 2$ either. However, appropriate identification of the universality classes of $D = 2$ critical behavior with conformally invariant theories often allows to extract the exact values of critical exponents. In Refs. [9] this was successfully performed for the $D = 2$ copolymer star of two or more mutually avoiding bunches of SAWs and RWs. Here, we analyze a copolymer star of one or two RWs or SAWs of species 1 and a bunch of f_2 RWs of species 2. In the notation of the above equations the following exact expressions for the corresponding exponents are derived from Refs. [9]:

$$\lambda_{1,f_2}^G = \frac{4f_2 + 1 + a}{8}, \quad \lambda_{2,f_2}^G = \frac{12f_2 + 11 + 5a}{24}, \tag{4}$$
$$\lambda_{1,f_2}^U = \frac{12f_2 - 13 + 2a}{24}, \quad \lambda_{2,f_2}^U = \frac{12f_2 - 16 + 5a}{24}, \tag{5}$$

with $a = \sqrt{24f_2 + 1}$.

As far as this is not an exact solution in terms of the original theory but rather an "exact conjecture" for the exponents we performed one more check of the scaling exponents by a MC simulation for the simplest case when the copolymer star consists of RWs only ($\lambda_{1,f_2}^G, \lambda_{2,f_2}^G$). In these simulations the stars are grown on a square lattice until a non-allowed intersection occurs. The number of stars $C(N)$ generated during the growing process is accumulated for all chain lengths N. Exponents are extracted assuming a power law $C(N) \sim N^{-\nu_0 \lambda_{f_1,f_2}}$ where the RW correlation length exponent is $\nu_0 = 1/2$. We generate stars up to a maximum chain length $N_{\max} = 10^3$ and accumulate configurations until $C(N_{\max}) = 10^5$. The

number of successful attempts to grow stars with longer chains decreases rapidly for higher $f_1 + f_2$ which increases simulation time drastically. While for the case $1 + 1$ a total of 10^6 attempts were needed, this number rose to $5 \cdot 10^9$ for $5 + 1$. Therefore, we report results only for $f_1 + f_2 \leq 6$. From the bare simulation data we extracted the numerical values of the exponents by an extrapolation to $1/N \to 0$. In Table I we report the results and the statistical error of this extrapolation in the lines marked 'MC' and '$\pm\Delta$'. We compare with the exact numbers according to Eqs. (4). The results are in fair agreement with a slightly growing discrepancy as the number of RWs f_2 increases.

In Fig. 1 we compare the results with the perturbative data of the ε-expansion naively adding successive orders of the perturbation theory series (2). We show the ε^2- and ε^3-approximations. The values predicted by successive orders of the ε-expansion for $\varepsilon = 2$ do not seem to correlate with each other nor with the exact values of the $d = 2$ exponents. It is not only the large expansion parameter $\varepsilon = 2$ that spoils the convergence of the perturbation theory. As is well known, the perturbation theory series of renormalized field theory are asymptotic at best [16] and have zero radius of convergence [17]. An appropriate resummation technique must be used to extract reliable data from the series. Here we use a Borel resummation refined by a conformal mapping [15] as described for this particular case in Ref. [7].

The resummation procedure allows us to restore convergence of the ε-expansion and enables us to extract reliable exponent values. These are also shown in Fig. 1. The same resummation is applied for the renormalization group expansions at fixed $D = 2$ [14]. All data is summarized in Table I. For $\lambda_{1,2}^G$ perturbation theory gives the exact result at first order with all higher orders vanishing [18]. For completeness we have included here as in Table II the corresponding $D = 3$ dimensional results from [7].

Table II contains the data for the resummed values of the exponents λ_{2,f_2}^U for the combined SAW and RW copolymer stars. We show the values obtained by the fixed $D = 2$ technique and the ε-expansion in comparison with their exact counterparts (5). Again, the results are in fair agreement for not too large numbers of chains f_2. Indeed as one can see from the formulas (2)–(3) the increase of f_2 leads to an increase of the ε-expansion coefficients resulting in a growing inaccuracy even of the resummed series.

In the perturbative treatment (which starts from the upper critical dimension $D = 4$ [2]) the order of the chains in the star does not matter for the scaling laws: there is always a possibility for every chain to interact with any other chain constituting a star. On the other hand, in $D = 2$ the order of chains does matter: each chain of the star will interact only with its direct neighbors. This topological restriction has to be taken into account when comparing exact and perturbative results for $D = 2$ linked polymers.

The data of Tables I, II convinces us that the perturba-

tion theory series for low numbers of chains f_2 is reliable even for $D = 2$. Also, we note that the $D = 2$ copolymers with $f_1 = 2$ are worse described by the perturbation theory than those with $f_1 = 1$ where the topological restriction is not present, due to the symmetry of ordering.

b. Multifractal Spectrum It is of special interest to notice another physical interpretation for the copolymer star exponents (1). For the diffusion of freely moving particles in the presence of a polymer absorber it may be shown [10] that the moments of particle density display universal scaling laws in the vicinity of the absorbing polymer. In particular, the nth moment $\langle \rho^n \rangle$ at distance r from the core of an absorbing polymer star with m chains scales as [7, 10]:

$$< \rho^n(r) > \sim (R/r)^{-\lambda_{m,n}}, \qquad (6)$$

here $< \ldots >$ denotes the ensemble average over the configurations of the absorbing polymers while otherwise we use the notations of formula (1). The harmonic measure that corresponds to this absorption phenomenon possesses multifractal [10, 11, 12] properties: The flux ϕ of diffusing particles onto the polymer star is interpreted as a measure defined on the fractal structure of the star polymer. This flux is proportional to the particle density (6) some small distance ℓ away from an absorbing point on the star polymer. The following scaling law for the normalized moments of the harmonic measure at the core of the star polymer is derived:

$$< \phi^n > / < \phi >^n \sim (R/\ell)^{-\tau_{m,n}}. \qquad (7)$$

Comparing formulas (6) and (7) the obvious relation between the exponents τ and λ is:

$$\tau_{m,n} = \lambda_{m,n} - n\lambda_{m,1}. \qquad (8)$$

Note, that here we use the standard definition [10] for the spectrum of the exponents τ, including normalization of the nth moment of the flux in (7) by $< \phi >^n$. The expression (7) is a multifractal measure as far as the spectrum τ is non-trivial ($\tau \neq 0$). Obviously, the spectrum λ is non-trivial as well, as one can see already from the second order perturbative results (2), (3): $\lambda_{mn} \neq n\lambda_{m1}$.

Using the relation (8) we now compare the values of the exponents τ as obtained in the perturbative approach with those of the MC simulations and the exact calculations. If the absorbing polymer star is chosen to be RW-like, then the spectra τ are calculated by substituting the exponents λ^G into (8) (and exponents λ^U for SAWs, correspondingly). We show in Fig. 2 the resulting spectra for the spectrum of the exponents τ_{1n}^U for the absorption at the end-point of a SAW. Again, we display the exact results derived from formulas (4) in comparison with the perturbative data with and without resummation. We observe a similar behavior as for the spectra λ: for low enough values of n the resummed perturbative renormalization group results are in reasonable agreement with the exact predictions.

The description of multifractal phenomena often uses the spectral function formalism [12]. To obtain this function for the absorption process on the center of a star of m chains we analytically continue the set of exponents τ_{mn} in the variable n and calculate the following Legendre transform

$$f_m(\alpha_{mn}) = -\tau_{mn} + n\alpha_{mn} + d(1 - n), \qquad (9)$$
$$\alpha_{mn} = \frac{d\tau_{mn}}{dn} + d.$$

According to the standard definition [10] we have included into (9) the fractal dimension d of the absorber. In particular, this gives the maximal value of the spectral function to be equal to $d - \tau_{m0} \equiv d - \lambda_{m0}$. There appears to be no natural generalization of d for arbitrary m. In our presentation we use that the fractal dimension of a polymer star is equal to that of a polymer chain ($d = 2$ for a RW and $d = 4/3$ for a SAW in $D = 2$, correspondingly). Another way to define the multifractal spectrum is chosen in Refs. [9] where the nth moments (7) are normalized not by $< \phi >^n$ but by $< \phi >$. This choice has the remarkable feature that without introducing an additional dimension d in (9) the maximum of $f(\alpha)$ $d = 4/3$ for both the SAW and the RW absorbers with $f_1 = 2$. However, this definition is not general, as already in $D = 3$ it does not lead to the correct location of the spectral function maximum.

We display the spectral function for the case of the absorption at a RW end in Fig. 3. The spectral function is negative for some values of α. This behavior was observed already in the perturbative studies of Ref. [10] and related to the ensemble average in formulas (6), (7) in contrast to the usual site average over the support of the measure. Comparing the perturbative, the MC and the exact results we note that the region of $1 < n < 5$ in which reasonable agreement for the spectra λ and τ is found corresponds to a rather small region in terms of the parameter α in the left wing of the spectral functions.

c. Conclusions The field theoretical description of a polymer network of different species has been derived recently [7, 8] in the form of renormalization group perturbation theory series. In this paper, we compared and verified the perturbation expansions for $D = 2$ with a subsequently published exact study [9] and MC simulations. We found that the series when appropriately resummed give a reliable description of the scaling of copolymer stars with not too many chains even for the $D = 2$ dimensional case. Not only the increase of the expansion parameter forbids application of the perturbative results for higher numbers of chains: in $D = 2$ topological restrictions appear that are not taken into account by field theory.

We have analyzed the multifractal properties of the resulting spectra of exponents and found that the spectrum $\tau(n)$ is in much better coincidence with the exact counterpart than the spectral function $f(\alpha)$. In the latter case the perturbative approach gives comparable results only for a narrow region in the left wing of the spectral

function. Note however, that the right wing corresponds to negative values of n, where obviously the analytic continuation of the perturbative expansions as well as of the exact results is speculative.

Acknowledgments

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[1] P.-G de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca and London, 1979).

[2] J. des Cloizeaux, G. Jannink, *Polymers in Solution.* (Clarendon Press, Oxford, 1990); L. Schäfer, *Excluded Volume Effects in Polymer Solutions* (Springer, Berlin, 1999).

[3] H. Kleinert, *Path Integrals in Quantum Mechanics, Statistics and Polymer Physics* (World Scientific, Singapore, 1995).

[4] J.-F. Joanny, L. Leibler, and R. Ball, J.Chem.Phys. **81**, 4640 (1984); J.F. Douglas and K.F. Freed, J. Chem. Phys. **86**, 4280 (1987); L. Schäfer and Ch. Kappeler, J.Phys.(Paris) **46**, 1853 (1985); Colloid Polym.Sci. **268**, 995 (1990).

[5] B. Duplantier, J. Stat. Phys. **54**, 581 (1989); L. Schäfer, C. von Ferber, U. Lehr, and B. Duplantier, Nucl. Phys. B **374**, 473 (1992); C. von Ferber and Yu. Holovatch, Cond. Matt. Phys., iss. 5, 8 (1995); Theor. Math. Phys. **109**, 34 (1996) [Engl. ed.: p.1274].

[6] B. Duplantier, Phys. Rev. Lett. **57**, 941 (1986); B. Duplantier and H. Saleur, Phys. Rev. Lett. **57**, 3179 (1986); H. Saleur, J. Phys. A **19**, L807 (1986).

[7] C. von Ferber and Yu. Holovatch, Phys. Rev. E **56**, 6370 (1997).

[8] C. von Ferber and Yu. Holovatch, Cond. Matt. Phys. iss. 10, 9 (1997); Europhys. Lett. **39**, 31 (1997); Physica A **249**, 327 (1998); Phys. Rev. E **59**, 6914 (1999); J. Mol. Liq. **93**, 155 (2001), ; C. von Ferber, Yu. Holovatch, A. Jusufi, C. N. Likos, H. Löwen, and M. Watzlawek, J. Mol. Liq.**93**, 151 (2001).

[9] B. Duplantier, Phys. Rev. Lett. **82**, 880 (1999); Physica A **263**, 452 (1999).

[10] M. E. Cates and T. A. Witten, Phys. Rev. A **35**, 1809 (1987).

[11] H. G. E. Hentschel and I. Procaccia, Physica D **8**, 435 (1983).

[12] T. C. Halsey, M. H. Jensen, L. P. Kadanoff, I. Procaccia, and B. I. Shraiman. Phys. Rev. A **33**, 1141 (1986).

[13] The third possibility when both species 1 and 2 behave as SAWs reduces [4] to the homogeneous star [5].

[14] In this case the expansion is performed in a "pseudo-ε" parameter, as explained e.g. in: [15].

[15] J. C. Le Guillou and J. Zinn-Justin, Phys. Rev. B **21**, 3976 (1980).

[16] see e.g. J. Zinn-Justin, *Quantum Field Theory and Critical Phenomena* (Oxford University Press, 1996); H. Kleinert, V. Schulte-Frohlinde, *Critical Properties of ϕ^4-Theories* (World Scientific, Singapore, 2001).

[17] G. Hardy, *Divergent Series* (Oxford University Press, 1948).

[18] A. N. Semenov, J. Phys. France **49**, 1353 (1988)

$f_1; f_2$	1;1	1;2	1;3	1;4	1;5	2;2	2;3	2;4	2;5
exact	1.25	2	2.693	3.356	4	2.916	3.738	4.510	5.25
MC	1.251	1.986	2.662	3.295	3.908	2.913	3.703	4.506	–
$\pm\Delta$	0.004	0.004	0.005	0.015	0.022	0.005	0.030	0.039	–
$D=2$	1.22	2.00	2.58	3.04	3.43	3.45	4.59	5.52	6.34
ε^3	1.20	2.00	2.56	2.99	3.36	3.41	4.49	5.37	6.13
$D=3$	0.58	1.00	1.35	1.69	1.98	1.81	2.53	3.17	3.75
ε^3	0.56	1.00	1.33	1.63	1.88	1.77	2.45	3.01	3.51

TABLE I: Exponents $\lambda^G_{f_1,f_2}$ (f_1 RWs and f_2 RWs) calculated by different techniques. Lower part: $D=3$ results.

$f_1; f_2$	1;1	1;2	1;3	1;4	1;5	2;1	2;2	2;3	2;4	2;5
exact	.38	1.04	1.67	2.28	2.88	.88	1.79	2.61	3.39	4.13
$D=2$	0.34	1.01	1.54	2.02	2.41	0.72	1.85	2.80	3.64	4.39
ε^3	0.32	1.03	1.57	2.01	2.41	0.76	1.87	2.82	3.62	4.34
$D=3$	0.15	0.51	0.81	1.07	1.32	0.42	1.02	1.57	2.05	2.49
ε^3	0.17	0.53	0.81	1.09	1.36	0.42	1.04	1.63	2.15	2.65

TABLE II: Exponents $\lambda^U_{f_1,f_2}$ (f_1 SAWs and f_2 RWs) calculated by different techniques. Lower part: $D=3$ results.
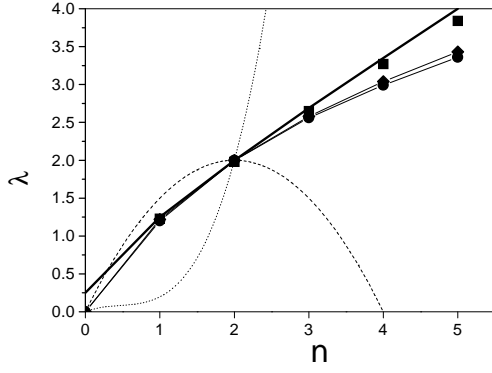
FIG. 1: Exponent $\lambda_{1,n}^G$. Lines: exact (bold), bare ε^2 (dashed), and ε^3 (dotted) data. Symbols: MC ($\blacksquare$, size is larger than errorbars); the resummed ε^3 ($\bullet$), and $D = 2$ data ($\blacklozenge$) are connected by thin lines.
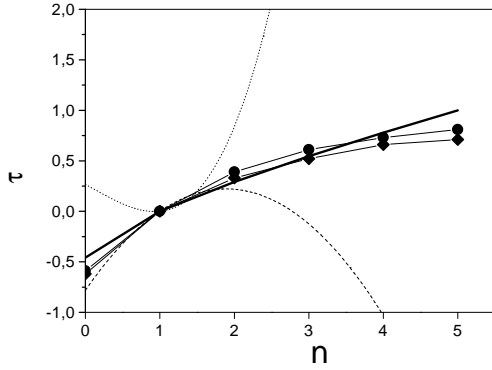

FIG. 2: The spectrum of exponents τ_{1n}^U for the absorption at the end of a SAW. Symbols as in Fig. 1.
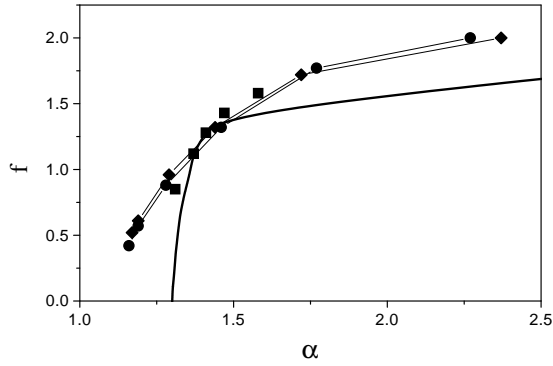

FIG. 3: The spectral function for the absorption at a RW end. Symbols as in Fig. 1.